EVALUATION ON FLOW BEHAVIOUR OF POLYPROPYLENE/KAOLIN COMPOSITES AT HIGH SHEAR STRESS

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by

SUZI SALWAH BINTI JIKAN

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Suzi Salwah Jikan

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LIST OF ABBREVIATIONS

$Al(OH)_3$ / ATH	Aluminium Trihydroxide
$Al_2O_3.2SiO_2.2H_2O$	Clay (Kaolin)
AO	Antioxidant
aPP	atactic PP
BE	backscattered electrons
C	Carbon
C(83-99%)	Carbon black
$CaCO_3$	Calcium Carbonate
$CaCO_3.MgCO_3$	Dolomite
CR	Polychloroprene
DETA	dielectric thermal analysis
DMTA	dynamic mechanical thermal analysis
DSC	differential scanning calorimetry
EDX	energy dispersive x-ray
EPDM	ethylene propylene diene monomer
FESEM	field-emission scanning electron microscopy
H	Hydrogen
HCPP	highly crystalline PP
HMS PP	High Melt Strength PP
iPP	Isotactic PP
$KM(AlSi_3O_{10})(OH)_2$	Mica
$KM(AlSi_3O_{10})(OH)_2$	Wollastonite
LCP	Liquid Crystal Polymers
MFI	Melt Flow Indexer
$Mg_3(Si_4O_{10})(OH)_2$	Talc
O	Oxygen
Org-MMT	organic-montmorillonite
PA	Polyamide
PC	Polycarbonate
PE	Polyethylene
PEEK	Polyetheretherketone
PEMA	poly[ethylene-co-(methylacrylate)

PET	Polyethylene Terephthalate
PMMA	Polymethyl Methacrylate
PP	Polypropylene
PP-g-MAH	PP/maleic anhydride grafted polypropylene
PPS	Polyphenylene Sulfide
PS	Polystyrene
PVC	Polyvinyl Chloride
R-TPO	reactor produced TPO
SE	secondary electrons
SEM	scanning electron microscope
Si	Silicon
SIC	shear-induced crystallisation
SiO_2	Precipitated silica
SiO_2 based	Glass fibre
sPP	syndiotactic PP
TG	thermogravimetry
TMA	thermomechnical analysis
TPE-O / TPO	thermoplastic polyolefins
UV	Ultraviolet

LIST OF SYMBOLS

μ, K , n	power law constants
ΔE	crystallization activation energy
ΔH	enthalpy
ΔS	entropy
μ	coefficient of viscosity
A	area
B_{swell}	extrudate swell ratio
d_d, D_{die}	die diameter
d_e	equilibrium extrudate diameter
$D_{product}$	product diameter
F	force
f(τ	function of shear stress
F(T)	kinetic parameter
G	shear modulus
K(T)	function of cooling rate
l	distance
L	length of die
L/D	length-to-diameter ratio
P	test pressure
Q	flow rate
r	reference
R	radius of die
t	time
T_g	glass transition temperature
T_m	melting temperature
T_p	programme temperature
T_p	crystallization peak temperature
T_r	represented temperature
T_s	transitional state temperature
v	velocity gradient
V_m	molar volume
W_f and W_s	constant instrument factors

$x = X_1$	downstream location
$x = X_2$	upstream location
X_{ma}	measurement terminating point
X_{min}	measurement of starting point
y	original depth
Z_c	half-time
Γ	shear strain
Δt	measuring time
Δx	deformation
ΔX	measuring stroke
ρ_m	melt density
T	shear stress
τ_y	yield stress

PENILAIAN KE ATAS KELAKUAN ALIRAN KOMPOSIT POLIPROPILENA/KAOLIN PADA TEGASAN RICIH TINGGI

ABSTRAK

Dalam penyelidikan ini, komposit polipropilena (PP)/kaolin telah dihasilkan secara penyebatian menggunakan penggiling berpenggulung-dua panas sebelum proses pengekstrudan melalui reometer kapilari dilakukan agar dapat memperbaiki sifat-sifat reologi sampel. Manakala, ekstrudat daripada alatan indeks aliran lebur (MFI) dianalisa bagi pengiraan ketumpatan leburan. Ketumpatan leburan mengalami pengurangan linear dengan peningkatan suhu pemprosesan dan menokok sedikit dengan kehadiran pengisi kaolin. Di dalam kajian sifat-sifat aliran lebur, kelakuan terma, analisis morfologi dan fenomena likat kenyal pula, komposit PP/kaolin telah diekstrud menerusi reometer kapilari. Kelakuan aliran keseluruhan sampel menunjukkan bahawa sistem berkelakuan pseudoplastik dalam satu julat kadar ricih tetapi dilatan dalam julat yang lain. Kesan pengaruh kandungan kaolin, suhu pemprosesan dan tegasan ricih terhadap penghabluran keseluruhan sampel, termasuk kelakuan isoterma dan tak isoterma, dikaji menerusi kalorimetri imbasan pembezaan (DSC). Hasil ujikaji menunjukkan peningkatan kandungan kaolin, suhu pemprosesan dan tegasan ricih telah menganjakkan puncak penghabluran eksoterma pada suhu yang lebih tinggi dan mempercepatkan masa penghabluran keseluruhan. Pengiraan tenaga pengaktifan penghabluran menerusi kaedah Kissinger pula mempamerkan suatu pola penurunan terhadap peningkatan kandungan kaolin, suhu pemprosesan dan tegasan ricih. Kajian terhadap aktiviti penukleusan menunjukkan pengisi kaolin mempunyai pengaruh penukleusan yang kecil pada matriks PP.

Pemerhatian terperinci pada kesan penukleusan juga menunjukkan kehadiran kaolin berserta kenaikan suhu dan tegasan ricih membolehkan penukleusan heterogen berlaku di dalam sistem. SEM dan EDX telah digunakan untuk analisis morfologi ekstrudat bagi mengkaji kesan tegasan ricih, suhu proses dan kapasiti pengisi. Mikrograf keratan rentas ekstrudat dianalisa untuk memperolehi nilai penyerakan dan taburan pengisi. Penyerakan dan taburan pengisi yang lebih sekata diperolehi apabila tegasan ricih dan suhu pemprosesan meningkat. Bagaimanapun, muatan pengisi yang terlalu tinggi boleh mengakibatkan penyerakan dan taburan pengisi yang tidak sekata. Kajian terhadap pembengkakan ekstrudat menunjukkan nisbah pembengkakan ekstrudat berkurangan dengan peningkatan suhu pemprosesan dan muatan pengisi pada tegasan ricih yang ditetapkan. Bagaimanapun, kajian terhadap kesan tegasan ricih dan kadar ricih menunjukkan nisbah pembengkakan ekstrudat (B) bagi leburan berkurang secara linear dengan peningkatan tegasan ricih ketara dan kadar ricih hingga satu titik di atas kadar ricih kritikal ($1.8 \times 10s^{-1}$). Komposit PP/kaolin memperlihatkan suatu ciri ketidakstabilan aliran dan herotan hasil pengekstrudan selepas melalui dai pengekstrudan pada muatan pengisi yang rendah dan pada suhu pemprosesan yang rendah iaitu 165°C. Rupa permukaan keseluruhan sampel turut dipertingkatkan apabila tegasan ricih direndahkan. Rekahan leburan dapat dihindarkan apabila dai kapilari dengan nisbah L/D = 10 digunakan.

EVALUATION ON FLOW BEHAVIOUR OF POLYPROPYLENE/KAOLIN COMPOSITES AT HIGH SHEAR STRESS

ABSTRACT

In this study, Polypropylene (PP)/kaolin composite was compounded on a heated two roll-mill prior to testing via capillary rheometer in order to improve the rheological properties of the samples. Whereas, the extrudate from melt flow indexer (MFI) were analyzed to calculate their melt densities. The results showed that the melt density decreased linearly with an increase in processing temperature and it increased slightly with the addition of kaolin filler. On the other hand, for the investigation of melt flow properties, thermal behaviour, morphological analysis and viscoelastic phenomenon of PP/kaolin composite, the sample was subjected to extrusion process by means of capillary rheometer. The flow behaviour of all samples revealed that the system appears to be pseudoplastic over one range of shear rates but dilatant over another. The influences of kaolin content, processing temperature and shear stress on crystallization of all samples, including isothermal and nonisothermal crystallization behaviour were investigated by differential scanning calorimetry (DSC). The results showed that increasing kaolin content, processing temperature and shear stress have shifted the crystallization exothermic peak to higher temperature and reduced the overall crystallization time. The crystallization activation energy calculated using Kissinger's method displayed a decreasing trend with increasing kaolin content, processing temperature and shear stress. A study of nucleation activity revealed that kaolin filler had a slight nucleation effect on PP matrix. A thorough observation on nucleation effect also revealed that

the incorporation of kaolin in chorus with increasing temperature and shear stress have contributed to successive heterogeneous nucleation in the system. The morphological analysis of the extrudate was analyzed using SEM and EDX in order to investigate the effect of shear stress, processing temperature and filler loading. The extrudates were cross-sectioned, micrographed and analyzed in order to quantify filler dispersion and distribution. Better dispersion and distribution of fillers were obtained with increasing shear stress and processing temperature. However, increasing filler loading can lead to uneven filler dispersion and distribution due to the overloading of filler content in the system. The extrudate swell studies demonstrate that the die swell ratio decreases with an increase in processing temperature and filler loading at fixed shear stress. Nonetheless, the study on the effect of shear stress and shear rate showed that the die swell ratio (B) of the melts decreases linearly with increasing apparent shear stresses and shear rates only up to one point above the critical shear rate ($1.8 \times 10s^{-1}$). PP/kaolin composite exhibited a characteristic of flow instability and extrudate distortions upon exiting from extrusion dies at low filler loading and at low processing temperature of 165°C. It was also found that decreasing the shear stress improved the surface appearance of all samples. Lastly, the melt fracture tended to be suppressed when a capillary die with a high L/D ratio which is 10, was used.

CHAPTER 1

INTRODUCTION

1.1 Preface

Major types of thermoplastics are Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Polyvinyl Chloride (PVC), Polycarbonate (PC), Polymethyl Methacrylate (PMMA), Polyethylene Terephthalate (PET) and Polyamide (PA, Nylon). Commercial thermoplastics are classified according to their performance as "Commodity" (low performance, like PE, PP, PS and PVC), "Engineering" (like PC, Nylon and PET), or "Advanced" (highest performance, like liquid crystal polymers (LCP), polyphenylene sulfide (PPS) and polyetheretherketone (PEEK). Engineering and advanced polymers had been anticipated to undergo explosive growth but that did not transpire. In spite of that, plastics have been continuously growing throughout the last three decades, but mainly in the commodity category. Currently, commodity polymers amount to about 88% of the volume produced, engineering plastics about 12%, and advanced plastics is less than 1%. Although the prices of advanced polymers per kilogram are much higher than those of commodity polymers, their global value to the economy is still very small. Therefore, PP is chosen for this study since PP is one of the most widely used plastic commodity in many demanding applications (Favis and Therrien, 1991; Wei *et al.*, 2000). It has many advantages as a base matrix for thermoplastic composites owing to its relatively low cost and high chemical resistance coupled with ease of fabrication. The good balances between mechanical and thermal properties of polypropylene, as well as its good performance in processing and practical applications lead to this material being widely used in industry and daily life. However, the range of

application is rather limited due to its poor impact toughness (Li *et al.*, 2009; Scheirs, 2000). An alternative way to increase the matrix toughness and to improve some of its properties is by introducing inorganic particles such as kaolin. Kaolin is in a group of clay mineral. Clay mineral is the group of important hydrous aluminum silicates with a layered structure and very small (microscopic) particle size. Kaolin in nature is normally in the form of hexagonal disks. They are constructed by laying double sheets of alumina octahedra and silica tetrahedra on top of one another (Trakoonyingcharoen *et al.*, 2006).

The past decade had seen great development of researches on polypropylene/clay composite since this material can offer enhanced fire, mechanical and barrier properties compared to polypropylene composites containing traditional fillers (Nitta *et al.*, 2006). The development of PP composites incorporated with inorganic fillers such as clay has initiated various activities focusing on the technology of polymer composites in its multifaceted applications (Chang *et al.*, 2007). In spite of that, there are problems encountered in the process of determining the accurate formulation for PP composites, wherein, the correct prediction is needed in order to anticipate how the filler will affect the entire characteristics and mechanical properties of the polymer composite (Da Silva *et al.*, 2002; Maiti and Mahapatro, 1991). Mechanical behaviour, however, is influenced by rheological behaviour (Guriya *et al.*, 1997; George *et al.*, 1999). Molecular orientation which is closely related with flow behaviour, for example, has dramatic effects on the mechanical and crystallization properties of molded objects, fibers and films. This is the second important reason for studying polymer flow behaviour.

Furthermore, the introduction of clay particles in PP matrix would greatly affect the flow behaviour or processablility of PP/clay composites. It is connected with the resistance of these particles in processing and/or shaping of the composite. The processability of polymeric material is one of the important characterization in the field of rheology (Gahleitner, 2001; Lou and Harinath, 2004). Rheology is a field of science that studies fluid behaviour during flow-induced deformation. The subject of rheology is very important for both polymers and polymeric composites, and this is true for two reasons. Firstly, flow is involved in the processing and fabrication of such materials in order to produce useful products. Thus fluid rheology is relevant to polymer processing as it determines stress levels in operations such as extrusion, calendering, fiber spinning and film blowing. Similarly, rheology influences residual stresses, cycle times and void content in composite processing operations such as bag molding, compression molding and injection molding. Clearly, a quantitative description of polymer and composite rheology is essential for developing models of the various polymer processing operations. These models can be employed for process optimization and for predicting the onset of flow instabilities. As a solution, the rheological behaviour of PP/clay composites should be studied as they are closely associated with the problems. Nevertheless, not much attention has been paid on the incorporation of kaolin as filler in PP composites. The subsequent paragraph discussed on some of the inorganic fillers which is in the group of clay such as kaolin, montmorillonite and bentonite.

The properties of calcined and hydrous kaolin filled nylon 6,6 composites have been investigated with respect to particle size and surface treatment with an amino-silane coupling agent. Treated calcined kaolin filled nylon 6,6 exhibits

improved strength and elongation properties, which are influenced by the silane loading level relative to the filler surface area (Buggy *et al.*, 2005). Wang *et al.* (2007) have recently studied the orientation and relaxation behaviors of organic montmorillonite (OMMT) layers and PP chains during and after shear with different filler dispersion and rheological behaviors. The correlation of rheology–orientation–tensile property in PP/OMMT composites has been phenomenally elucidated in detail. Their results suggested that the rheological behaviors, such as alignment induced by larger-amplitude shear and stress relaxation, could be reliable references for appraising the orientation capability of the composite in practical injection-molded processing. The rheological response to shear and the disorientation kinetics play important roles in determining the orientation structure of molded bar and the tensile properties as well (Wang *et al.*, 2007). As reported by Galgali *et al.* (2004), the orientation of the clay tactoids in PP matrix increased with extrusion shear rate. Tensile modulus of the sample along the flow direction was measured and was found to correlate well with the average orientation of the clay tactoids.

The research done by Muksing *et al*. (2008) showed that the relationship between shear stress and shear rate of organobentonite-filled polypropylene composites was well described by the power law. The incorporation of organobentonite filler enhances the pseudoplasticity of polypropylene, i.e. the material becomes more shear-thinning. With increasing filler concentration, the shear viscosity increases while the power law index (n) decreases. The activation energy (E_a) decreases gradually with an increasing of shear rate and increases sharply with filler concentration at or above 3 wt%. Extrudate swell increases non-linearly with increasing shear rate, but increases linearly with increasing shear stress and/or

decreasing temperature. Lastly, with increasing organobentonite concentration (>3 wt%), the extrudate swell decreases, especially at higher shear rates, which is attributed to the limitation of the elastic recovery of the confined polymer chains by highly orientated silicate layers after capillary extrusion (Muksing *et al.* 2008).

Sun *et al.* (2009) studied the crystallization of PP/organic montmorillonite (OMMT) composite under shear field. It was reported that the shear flow could enhance the crystallization of PP/OMMT composite even though shear strain was small. The effect of shear on crystallization became stronger with the shear strain increasing. However, the crystallization of PP/OMMT composite was not influenced by shear flow after being sheared at 2.2 s^{-1} for 10 s and the crystallization behavior was similar with that of the un-sheared sample because the filler network in PP/OMMT composite was not destroyed under small shear strain. When shear strain was large enough to destroy the filler network and align the clay layers along the flow direction, then oriented crystals including cylindrites and strings of spherulites were formed. These aligned clay layers acted as heterogeneous nucleation agents to promote crystallization of PP (Sun *et al.*, 2009). The type and degree of molecular or filler orientation are largely determined by the rheological behaviour of the polymer and the nature of the flow during fabrication process (Gupta *et al.*, 2005; Maity and Xavier, 1999).

Melt flow behavior tests, such as the melt flow indexer (MFI) test, capillary rheometer and torque rheometer are generally used to characterize the rheological behaviour of a material. These studies can then be utilized to establish better processing conditions and to develop optimum morphology to maximize products

performance (Han, 1976). Although all these (and other) studies have contributed to our fundamental understanding of the subject, industrial applications still cannot directly benefit from them. This is partly due to the fact that the results are either too theoretical or the conditions in which they have been investigated are too far away from actual industrial practices. Thus, the flow studies in this research work only utilize capillary rheometer because the shear rates used by this equipment range from 10 to 10^6 sec^{-1}. This range falls within the same range as those involved in polymer processing operations, such as injection moulding and extrusion.

The rheological behaviour of polymeric materials is closely related to viscoelastic and viscoplastic behaviour. Superposition of viscoelastic and viscoplastic effects in non-Newtonian flow are often evident if the dispersion medium is a viscoelastic melt. This is observed in filled polymers with active (structure forming) filler. Discussion on flow behaviour does not end here; it will be discussed comprehensively in Chapter 2.

1.2 Problem Statement

The development of polypropylene composites has recently given rise to various activities focusing on polymer technology in its multi-faceted applications (Nam *et al.*, 2001). However, there are challenges encountered in determining the right formulation for the filled polypropylene wherein the right prediction is required in order to anticipate how the filler will affect the overall characteristics and performance of the polypropylene composites. In order to overcome this problem, rheological features for polypropylene composites should be studied since it is closely related to the situation at hand. Research on polymer composite rheology is

really important for two main reasons; the first reason being the melt flow of any material is very relevant to processing particularly understanding the stress level of the melt flow in an operation to manufacture a useful product. The second reason is due to the fact that the type of filler and polymer molecules orientations are determined by the natural rheological features of the polymer matrix and its natural flow during processing (Gupta *et al.*, 2005). To that effect, research regarding rheological behaviour of polypropylene composite should be reviewed since it is very important in ascertaining its mechanical characteristics which are widely known as being greatly influenced by its production history.

This study is restricted to capillary rheometer since it is valuable for steady-shear investigations at very high shear rates. The shear rates range used in capillary rheometer is 10 to 10^6 sec^{-1}. The results obtained in the experiment have direct implications since this range falls within the same range as those involved in polymer processing operations.

For the purpose of this research, kaolin was used as filler in polypropylene matrix. Kaolin was chosen for its variety of advantages namely lower in cost, its ability to provide stiffness from low to medium scale, and also other advantages during processing especially for extrusion and calendering. Effective function of filler is dependent on its shape, size and chemical structure. These are among the reasons why kaolin was chosen instead of other fillers such as calcium carbonate and silica. In addition, kaolin with its plate-like shape offers more interactable surface area compared to calcium carbonate which is cubic-shaped particles (Ray and Okamoto, 2003). By executing this research, the filler effect and precise formulation

can be predicted by studying the flow characteristics of PP/kaolin composites with the aid of capillary rheometer. Rheological characterisation for the filler system is a requirement in solving problems in plastic processing, in which the addition of filler is said to be able to change the processing condition of a material (Joshi *et al.*, 1994).

The processing temperature is also an important aspect in determining the melt flow behaviour of polymeric material, which is altogether crucial in determining the quality of final features of the product to be produced (Sombatsompop and Panapoy, 2000). The exact temperature to be used in polymer processing is essential because at high temperature, polymer is bound to degrade easier or unwanted side effects may occur. For some polymeric materials, temperatures required for processing are very crucial which leads to the necessity of knowing the exact processing temperatures.

1.3 Scope And Objectives Of The Study

In order to improve the competitiveness of PP in engineering applications, its properties have to be modified. This can be achieved by introduction of reinforcing filler, such as kaolin. In recent years, kaolin-filled PP composite has been recognized as one of the most promising research fields in polymeric material. They have attracted a great deal of interest because they demonstrate improved physical and flow properties in comparison to the pure PP and other PP composite such as calcium carbonate-filled PP composite. It is well known in the rheological world that a small amount of addition of such filler can cause significant changes in the flow properties (e.g. the viscosity of the base polymer). The purpose of this study is to develop a

rheological understanding on PP/kaolin composite as it can help us to optimise the processing condition of this polymeric material.

The prime objectives of this study are:

i. To observe the flow behaviour of kaolin-filled PP composite at different processing parameters such as kaolin loading, processing temperature and shear stress.
ii. To study the thermal and morphological analyses of kaolin loading, processing temperature and shear stress of PP/kaolin composite processed at high shear stress.
iii. To investigate the extrudate swell and flow instability that occurs during extrusion which processed at high shear stress.
iv. To observe the flow behaviour of kaolin-filled PP composite using capillary rheometer since it is valuable for steady-shear investigations at very high shear stress.

This research focuses on the flow behaviour of PP/kaolin composite at high shear stress. The first and second chapters focus on some basic definitions and concepts useful for the understanding of compounding and processing, flow properties, thermal and viscoelastic behaviour and finally morphological analysis of pure PP and PP composites. The materials and experimental procedures needed in determining a useful data for this research work are presented in the third chapter. Chapter four discusses the influences of kaolin loading and processing conditions such as shear stress and processing temperature observed for PP/kaolin composite

processed at high shear stress. The results and discussion sections are divided into four parts. The influences of kaolin loading and processing conditions are discussed thoroughly in terms of its flow, thermal, morphological and viscoelastic properties. Finally, the last chapter concludes with challenges and suggestions for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Polypropylene

The matrix used for this study is Polypropylene (PP). PP is a linear hydrocarbon polymer that contains little or no unsaturation in its chain structure. PP and PE have some similarities in their characteristics such as swell in solution. PP is a thermoplastic that has good performances in process and practical applications as well as low in price. It is used extensively in industrial and domestic products, namely automobiles, electronic appliances, vessels and tube, spinning and film, and so on (Hanna, 1990). The characteristics of PP vary according to the molecular weight and grade.

Polypropylene is a long chain polymer (refer Figure 2.1). Structurally, it is a vinyl polymer with every other carbon (C) atom in the backbone chain attached to a methyl (CH_3) group. PP can be made from the propylene monomer by a process known as Ziegler-Natta polymerization or by metallocene catalysis polymerization. In these polymerization techniques, the propylene monomers with combination of two active metallic catalysts such as titanium chloride ($TiCl_3$) and triethylaluminum ($Al(eth)_3$), or better known as the 'Ziegler Catalyst', are exposed to heat and pressure. This is then combined with propylene monomer to form a long polymer chain, better known as PP. It is discovered that by using different types of catalysts and polymerization methods, the molecular configuration can be arranged to produce three types of PP.

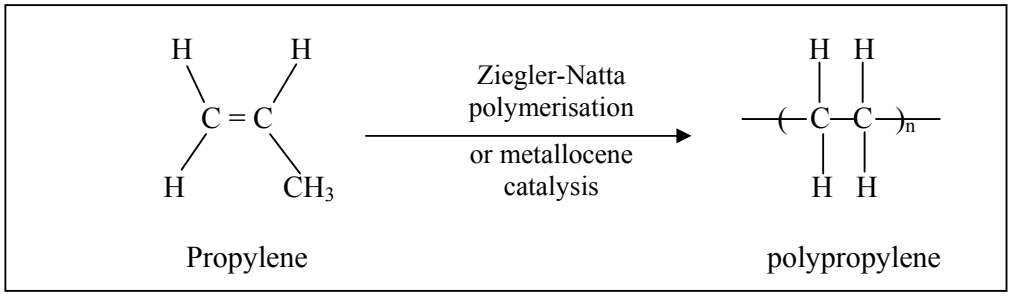


Figure 2.1: A simplified diagram for polymerization of polypropylene.

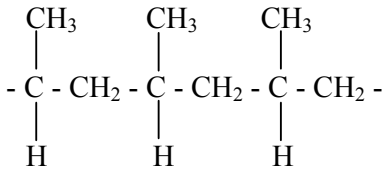
The presence of methyl group in PP backbone chain can provide various differing characteristics for PP, depending on the arrangement of methyl group in PP carbon atom, whether in isotactic, syndiotactic or atactic configuration (as shown in Figure 2.2). The mechanism of incorporating propylene monomer into long polymer chain of PP produced various polypropylenes of differing tacticities (Rothon, 2003):

i. Isotactic – identical configurations for all monomeric units.
ii. Syndiotactic – alternating configurations for monomeric units.
iii. Atactic – random configurational sequence of monomer units.

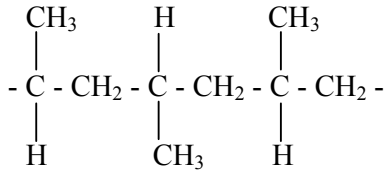
Isotactic PP (iPP) has all methyl groups arranged in the same configuration. Most (90-95%) of commercial PP are iPP produced with Ziegler-Natta catalyst with head-to-tail incorporation of propylene monomer. iPP has the ability to crystallize in order to offer better mechanical characteristics (Somani *et al.*, 2000). Isotactic configuration is the most stable structure since the methyl group is arranged at only one side in the PP chain structure. This structure prevents PP from crystallizing in a zig-zag planar shape, but rather in helical crystal structure. The degree of crystallization can normally reach up to 50%. The isotactic configuration also causes an increase in PP softening temperature. However, the presence of methyl group

enables PP to be easily oxidized and prone to chemical attack by certain chemical agents, especially at β hydrogen atom which is attached to methyl group.

(a)



(b)



(c)

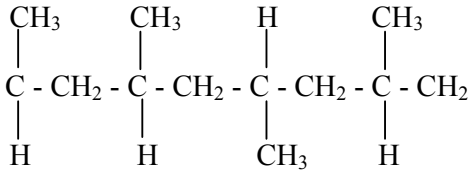


Figure 2.2: The three basic structures for polypropylene (a) isotactic, (b) syndiotactic and (c) atactic.

On the other hand, methyl group in syndiotactic PP (sPP) is arranged alternatingly along the backbone chain of PP. sPP demonstrates polymorphism characteristic which is caused by lower crystallization temperature and did not display helical crystal structure as shown by iPP. Atactic PP (aPP), in contrast, has a random methyl group configuration. The irregularity of aPP greatly affects the characteristics of aPP end products. aPP is unable to crystallize and produce softer

products such as candles, and does not have any useful mechanical traits (Frank, 1968).

Table 2.1: Characteristics of isotactic, syndiotactic, and atactic PP (Frank, 1968).

Characteristic	iPP	sPP	aPP
Density (g/cm^3)	0.92 – 0.94	0.89 – 0.91	0.85 – 0.90
Melt Level (°C)	165	135	-
Solubility in hydrocarbon at 20°C	Undissolved	Low	High
Yield strength	High	Medium	Very Low

The tacticity of macromolecules influences the degree of hardness, crystallization, amorphous and flexibility of backbone chain. PP is a crystalline thermoplastic in isotactic and also syndiotactic forms whilst atactic is amorphous and rubbery. iPP which is the most stereo-regular structure of PP, has been recognized as commercially important since it provides high degree of crystallinity. As a result, many mechanical properties and processability of PP are heavily determined by the level of isotacticity and thus crystallinity (Frank, 1968). Mechanical, solubility and melt level can be ascertained with knowledge on polymer tacticity. Most commercial PPs comprised 90-95% isotactic configuration. However, Cheng *et al.* (2004) reported that commercial PP is known to possess only 60-70% crystallinity, due to large amount of atactic PP in the production scale grades. The atactic PP reduces the ability of isotactic PP from achieving maximum crystallinity (Cheng, 1986).

The above discussion only takes into consideration the common PP typically used in various industries. However, PP is actually produced in many forms such as homopolymer, copolymer with ethylene, or homo- or copolymer blended with

ethylene propylene diene monomer (EPDM) rubber, to improve substantially low temperature impact resistance. It is known as thermoplastic polyolefins (TPE-O or TPO, when elastomeric properties appear at higher levels of EPDM). In recent development of PP, several major PP producers have produced reactor TPO (R-TPO). This reactor produces PP during polymerization. The advantage of R-TPO is it reduces manufacturing cost. In addition, Montell has also produced "High Melt Strength" (HMS) PP, with highly branched PP chain, which improves foaming, extrusion and blow moulding. Recently, highly crystalline PP (HCPP) has also been developed which demonstrates improved stiffness, heat and scratch resistance due to high level of crystallization. It can also substitute 10-15% mineral filler PP composites whilst offering the advantages of lower density and better surface aesthetics (Karian, 2003). This is only a brief discussion on the latest development of commercial engineering plastics. The main discussion will be on common PP since it is used in this research work.

Polypropylene, like many other thermoplastics, has its own set of unique characteristics. Generally, PP is a plastic that is cheap, lightweight, translucent and tough. PP also has satisfactory mechanical characteristics. Other than that, PP displays resistances towards chemical, fatigue, dampness, environment stress-cracking and good dielectric characteristics. PP can also be continually used at temperatures as high as 104^{o}C (Rothon, 2003). The following list entails some typical characteristics of PP that are considered advantageous and disadvantageous (Hanna, 1990). Among the advantageous characteristics are:

i. Requires no drying to process

ii. Low cost (per unit volume)

iii. Excellent toughness/ stiffness balance

iv. Excellent fatigue resistance

v. Good optical properties

vi. Great range of special purpose grades

vii. Excellent chemical resistance

viii. Lower density

ix. Excellent dielectric properties

x. Excellent moisture barrier

While the disadvantageous characteristics of PP are :

i. Low-temperature brittleness

ii. High thermal expansion

iii. Flammability

iv. Poor UV resistance

v. High mould shrinkage

vi. Reduced extruder output

vii. Low resistance to weathering

viii. Low impact strength

ix. High sensitivity to oxidative degradation

x. Haziness

xi. Difficulty in printing, painting and gluing

xii. Low melt strength

The ability of PP to be recycled has made it a versatile thermoplastic commodity (Kaempfer et al, 2002) and PP, being a semi-crystalline thermoplastic, is one of the most used thermoplastics in the industry. Its ease of processing, resistance to chemicals, low density (typically 0.91 g/cm^3) and relatively low cost enable it to be utilized in diverse industrial applications (Azizi and Ghasemi, 2004). However, its usage in engineering applications is rather limited due to its high shrinkage rate and relatively poor impact properties at room temperature, caused by its high glass transition temperature and high degree of crystallinity (Liang, 2002). In order to resolve this constraint, PP properties need to be altered, specifically by introduction of reinforcing filler into PP (Guerrica-Echevarría *et al.*, 1998 and Kaempfer *et al.*, 2002). Thus so doing, increase in PP strength, stiffness, electrical and thermal conductivity, hardness and dimensional stability can be customized. Another major objective for developing these new plastic materials, namely composites, is to obtain polymeric products with low manufacturing costs (González *et al.*, 2001).

2.2 Definition And Classification Of Composites

Composite materials are produced from the combination of two or more materials of different properties. The materials work together and produce composites with unique properties (Callister, 2000). Polymer composite can be defined as a mixture of polymer with inorganic or organic additives such as long fibres or discontinuous (short) particulates (flakes, platelets, spheres or irregulars) having certain geometries,. These additives are dispersed throughout the continuous matrix (Karian, 2003). Composite materials contain two phases, which are the dispersed and matrix phases. These phases are separated by a thin layer called interface phase. Both phases sustain their individual characteristics in the composite.

End characteristics of composite materials produced are unique and cannot be demonstrated by any component individually.

Composites are considered as a standard option for structural applications when high performances are necessary, and they represent an important class of engineering material. Polymeric matrix composites are irrefutably the most used among the large variety of composites. More and better polymer composites are now actively sought due to new requirement and new product. Engineering plastics with lightweight and high performance have replaced metals in many applications since polymers are relatively cheap. The wide applications of polymer composites range from the manufacturing of engineering structures such as tanks, pipes, aircraft interior furnishings and support beams, to the production of leisure and sports items such as golf clubs and balls, skis, racquets and boats (Karian, 2003).

Polymer composites can generally be divided into two broad classes which are thermoset and thermoplastic composites. The importance of thermoplastic composite has increased in comparison with thermoset composite. In recent years, the development of new materials has been oriented towards thermoplastic composites, since they offer more attractive systems, with great significance for research and industrial application. An important commercial advantage is that thermoplastic composites offer a way to produce new materials, by using available raw mineral materials, faster processing and reducing developments cost. Thermoplastic composites also yield high plasticity and damage toleration characteristics compared to brittle thermoset system. The cost for producing products of particle reinforced thermoplastic composite is also cheaper than thermoset. In

addition, thermoplastic can be recycled by reheating process. Advantages and disadvantages of thermoplastic composites are as follows.

The main technological advantages of thermoplastic composites are:

i. Low production cycle time
ii. High toughness and impact resistance
iii. Reforming possibility
iv. High repairability
v. Joining and assembly by local fusion bonding
vi. Uncontrolled shelf life
vii. Recyclability and environmental protection
viii. Good chemical resistance

Whilst the main technological disadvantages are:

i. High processing temperatures
ii. High processing pressures
iii. Draping difficulties

Thermoplastic composites can be subdivided into two types, namely commodity and engineering. The first, commodity or microscopic composites, are produced using polymer as matrix phase or material containing polymer as matrix which surrounds or covers fibre and/or small filler. Dispersed phase is comprised of either fibre or particulate type. Whereas, engineering composites are composites

which consist of nano filler or continuous fibre as dispersed phase in polymer matrix having high performance characteristics (Cantero *et al.*, 2003a; Cantero *et al.*, 2003b; Felix and Gatenholm, 1991). These composites have high mechanical characteristics and are commonly known as the most developed polymer composites. It is classified as a high performance composite in order to differentiate it from other composites that use short fibres or other fillers (Callister, 2003; Sharma and Nayak, 2000).

Polymer composites can also be categorized into three main groups. The classification of these composites is generally shown as below:

i. Polymer-polymer combinations (polymer blends)
ii. Polymer-gas combinations (expanded, cellular or foamed polymers)
iii. Polymer-rigid filler combinations of:
    - Polymer-fiber
    - Polymer-particulate filler
    - Polymer-hybrid filler

Meanwhile, Callister (2005) classified in details the classes of composites namely structured reinforced composite, fibre reinforced composite and particle reinforced composite:

i. Structured reinforced composite

    - The strength of this composite is influenced by the characteristics of substances used and structured element in geometric design. Laminated and sandwich composites belong in this category.

ii. Fiber reinforced composite

- This composite is strengthened by fiber that has aspect ratio of at least 100 (with the fiber length and diameter in nm unit).

iii. Particle reinforced composite

- A dispersed particles act as reinforcing phase in this composite. Most commercial plastic products belong in this group.

Using the above classification, this study falls into the polymer-particulate filler category, wherein the polymer matrix used is polypropylene while kaolin is used as filler. The examples for common fillers are carbon black, mica, silica and calcium carbonate. Particulate filled polymer composite consist of plastic (matrix) filled with small particles (dispersed phase) in accordance with specific formulations. These filler particles are capable of modifying the composite characteristics corresponding to the type and percentage of filler added (Rothon, 2003). The dispersed phase is harder and stiffer than matrix. The level of mechanical characteristics is based upon the strength of the bond between interface matrix and filler (Callister, 2005). Thus, it is important to possess knowledge in polymer engineering, filler and surface science in order to produce good PP/kaolin composite. Good composite must have balance between its attributes and processing cost. Therefore, the filler that is incorporated into matrix should be suitable with its end application.

2.3 The Role of Filler in Composites Activity

Of late, the use of kaolin as filler in polymer composite has attracted more attention. However, before the essential features of kaolin can be further elaborated, the definition and important characteristics of filler should be discussed beforehand. This is vital so that the application or role of filler in composite can be utilized as much as possible. The incorporation of fillers into polymer can affect almost all of its property which include surface, colour, density, shrinkage, expansion coefficient, conductivity, permeability and mechanical (Rao *et al.*, 1998), thermal and rheological properties (DeArmitt and Rothon, 2002; Dutra *et al.*, 2000). Many factors influence the behaviour of fillers in polymer. The type, incorporation method and loading (Pukanszky and Maurer, 1995) of filler dictate its effectiveness. Furthermore, the most important features include particle size distribution, surface area, shape, colour, refractive index, impurities, density, hardness, moisture content, thermal stability, modulus, surface chemistry and toxicity (some of the features are presented in Table 2.2). The weight percentage of filler is often given, but the mechanical, physical and electrical properties of compound in fact depend on the volume percentage of filler. Modulus and yield strength, for example, vary linearly with the volume percentage of filler. Modulus of compound is found to increase with addition of filler since mineral fillers have substantially higher moduli than polymers. Higher modulus can also be contributed by high surface area and anisotropy. Yield strength is another key property. This property is closely related to particle size, surface area and shape of fillers.

Table 2.2: Key properties of some common fillers (DeArmitt and Rothon, 2002).

Filler	Shape	Density (g/cm^3)	Mohr hardness	Chemical formula	Colour
Calcium carbonate	Spherical	2.7	3	$CaCO_3$	White
Dolomite	Spherical	2.85	3.5	$CaCO_3.MgCO_3$	White
Talc	Platy	2.7	1	$Mg_3(Si_4O_{10})(OH)_2$	Grey/white
Mica	Platy	2.76-2.88	3-2.5	$KM(AlSi_3O_{10})(OH)_2$	White/brown
Wollastomite	Acicular	2.9	4.5	$KM(AlSi_3O_{10})(OH)_2$	White
Clay (Kaolin)	Platy	2.6	2.5-3	$Al_2O_3.2SiO_2.2H_2O$	White/brown
Glass fibre	Fibrous	2.59	6.5	SiO_2 based	Colourless
Carbon black	Spherical	1.7-1.9	1	C(83-99%)	Black
ATH	-	2.4	-	$Al(OH)_3$	White
Precipitated silica	Spherical	2.0	7	SiO_2	White

Of those mentioned, particle size distribution is especially one of the most important factors. Particle size is normally reported in median or average of a sample population. Generally, filler in most engineering polymer application requires size of particles that is less than 40 nm. Better reinforced phase could be produced with smaller particle size which is less than 3 nm (Abu-Zurayk *et al.*, 2009). Filler with fine particles will increase modulus strength and abrasion resistance. These fine particles can be very difficult to disperse. They form agglomerates that act as large particles. Agglomeration is one of the weaknesses for small size filler. These small particles can only demonstrate maximum filler characteristics when fillers are well-distributed in thermoplastic matrix (Fekete *et al.*, 2004; Fekete and Pukanszky, 1997). This determines how many particles exist at a given loading, how close to one another the particles will be, and how much filler surface there will be. All of these affect the properties of samples. Nonetheless, even when fine fillers are well-dispersed, the high amount of filler surface associated with fine particles can

adversely affect polymer structure, often leading to high stiffness but low toughness. Thus, it is crucial to identify the optimum particle size needed to be incorporated in the new polymeric product. The optimum particle size varies with application and polymer type.

Particle shape is another crucial factor in the incorporation of filler in polymer since this affects the polymer characteristics and processing method. According to Radosta and Trivedi (1987), particle shape influences the characteristics of flexibility, permeability and also flow characteristic of polymer composite. In addition, particle shape is also an important factor in determining the stiffness of composites (Rothon, 2003). Shapes of particles can be categorized as cubic, needle-like (acicular), block, plate or fibre. Spherical particles that flow and disperse well cause least problem with stress concentration (Premalal *et al.* 2002; Pukanszky, 1995). Needle-like (acicular), fibrous and platy particle shapes can be more difficult to disperse and they can act as stress concentrators, which reduces impact strength (Rothon, 2002). The aspect ratio value is often used to categorize particle shape. For plate-shaped particles such as kaolin, the aspect ratio value is the ratio of mininum diameter of the sphere that has the same area with plate surface of the thickness. The aspect ratio value can be used as parameter to calculate the density of filler in polymer (Zweifel, 2001). Almost all fillers are significantly denser than common polymers thus resulting in composites with increased density. This is often undesirable, but tolerated. Platy fillers especially fibrous fillers are able to reinforce such as enhanced yield strength. From study of PP/clay composite, clay with aspect ratio value of 17-35 had been reported as capable of increasing the composite mechanical attributes (Zhou *et al.*, 2005). In addition, particles with high aspect ratio

value can increase modulus, tensile strength and reduce extrusion shrinkage (Zhou *et al.*, 2005). Whereas, cubic and spherical particles produce the lowest reinforcing characteristics. Indeed, some researches reported that spherical fillers, dolomite for example, fails to reinforce composites at all (Rothon, 2003). Spherical fillers usually decrease the yield strength of the compound relative to the unfilled polymer, unless the particles have exceptionally high surface area. High surface area and anisotropy would increase the magnitude of reinforcement.

Most commonly used fillers are minerals that are ground rock and ores processed to obtain a material in particulate form. They do not cleave, part or fracture uniformly. As a result their particles are generally irregular in shape (Ferrigno, 1987). Most of modifications of polymer caused by mineral fillers are controlled by several factors such as mineralogical, chemical, and physical properties (Murray, 2000). Mineral fillers are natural substances that exist on earth and they have an important role in the polymer industry (Rothon, 2003). Most of the mineral fillers have been reduced in size using wet grinding technique. Apart from that, the processes of separation and surface treatment are also carried out to increase the suitability of filler with polymer matrix (Girard, 2009). Particulate mineral fillers include carbon black, talc, mica, kaolin and so on. The main reasons for using fillers are (Xanthos and Todd, 1996; Rothon, 2002; Pukanszky, 2005):

i. Overall cost reduction
ii. Improving and controlling of processing characteristics
iii. Density control
iv. Thermal conductivity